

# Femtosecond Hole Dynamics in Ge studied by femtosecond pump-probe reflectivity

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# Femtosecond Hole Dynamics in Ge

- Introduction:

- Why Germanium?
- Why reflectivity?

- Experimental Data:

- $\Delta R/R$ : Ge, 300 K, 1.5 eV,  $n=4 \times 10^{18} \text{ cm}^{-3}$ , 140 fs resolution

- Model: Drude reflectivity of the photoexcited carriers

- diffusion (temperature-dependent)
- carrier relaxation (Monte Carlo simulation: density, temp.)
- band gap renormalization (temperature-dependent)

- Conclusion:

- reflectivity changes  $\Delta R/R$  are due to HOLE DYNAMICS
- optical deformation potential:  $d_0=30$  to 35 eV

## Why Ge? Why reflectivity?

- Trivial reasons:

- Nobody has done it.
- Easier than transmission (bulk sample).

- Why is it interesting?

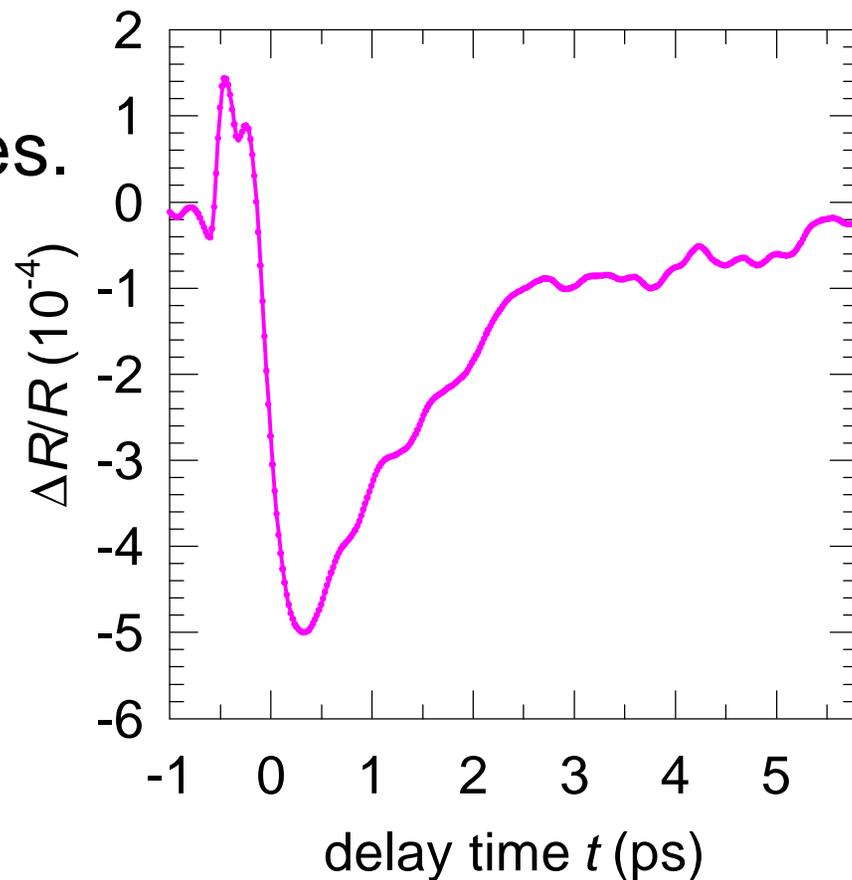
- $\Delta T/T$  due to electron-hole pairs in  $\Gamma$ -valley.
- Ge is indirect: Electrons disappear in 100 fs.
- Reflectivity measures Drude response.
- $\Delta R/R$  mostly due to hole dynamics.
- We know more about electrons than holes.
- Light hole to heavy hole scattering: Coupling of holes to optical phonons (deformation potential interaction).



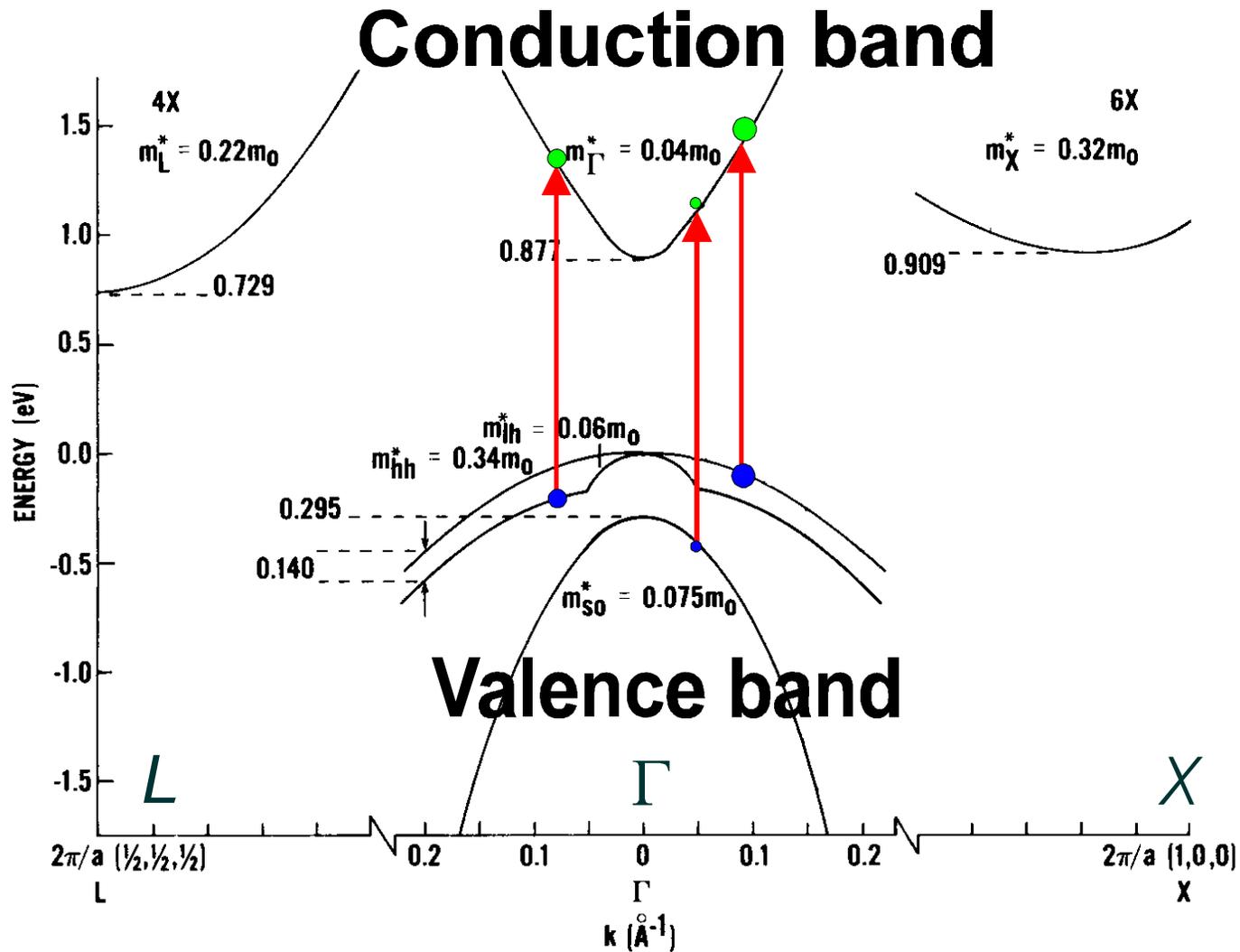
## Experimental Data:

bulk Ge, 1.5 eV, 140 fs pulses, 300 K,  $n=4\times 10^{18}$  cm<sup>-3</sup>

- Small increase for negative delay times.
- Fast decrease near  $t=0$ .
- Slow recovery, complete after about 5 ps.



# Photoexcitation of electron-hole pairs



## Reflectivity changes are due to:

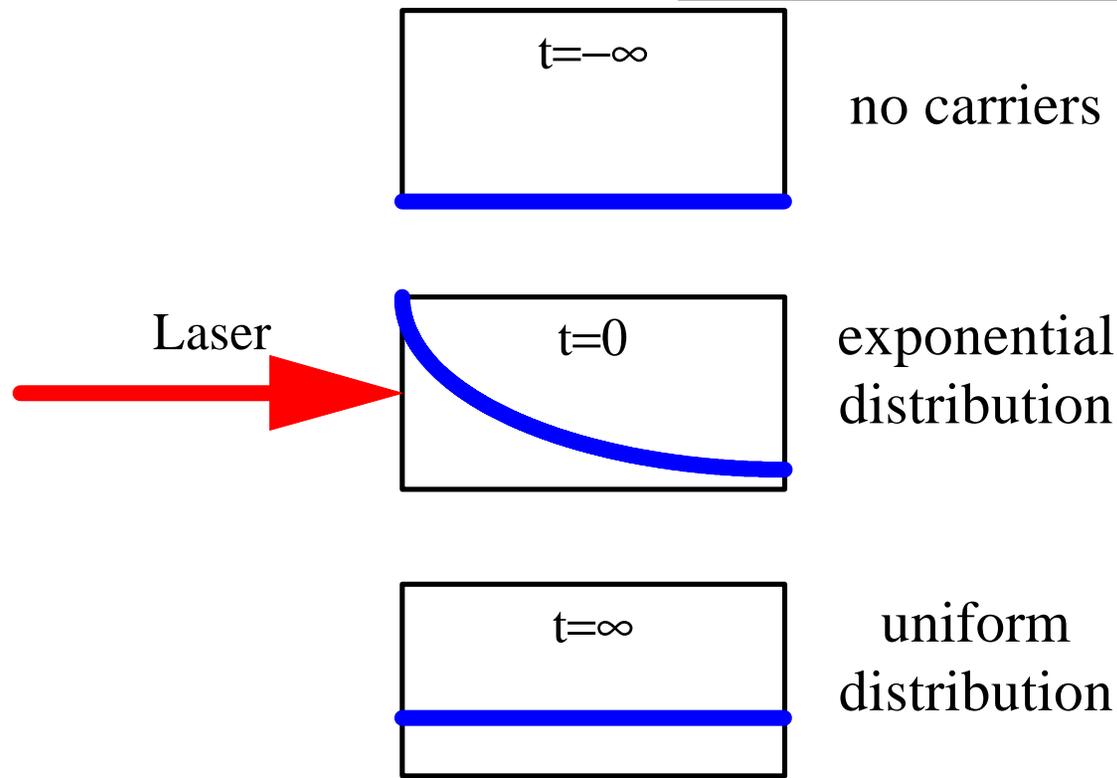
- Diffusion
- Relaxation:
  - Cooling of electrons and holes
  - Electron dynamics (intervalley scattering)
  - **Hole dynamics** (light hole to heavy hole)
  - Screening of carrier-phonon scattering
- Band gap renormalization:
  - Band gap shrinks with increasing density of electron-hole pairs.

# Diffusion:

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial z^2} - n - \frac{n^3}{3} + \frac{n_0 S}{\sqrt{t}} e^{-z^2/s^2 t}$$

$$n(z, t) = 0 \quad \text{at } t = -\infty$$

$$\frac{\partial n}{\partial z} = \frac{S}{D} n \quad \text{at } z = 0.$$



## Diffusion:     $S=0, \gamma_3 n^3 \cong \lambda n$

Diffusion equation:

$$\frac{n}{t} = D(t) \frac{\partial^2 n}{\partial z^2} - n + \frac{n_0 s}{\sqrt{t}} e^{-z - s^2 t^2}$$

Initial/boundary conditions:

$$n(z, t) = 0 \quad \text{at} \quad t = -\infty$$

$$\frac{\partial n}{\partial z} = 0 \quad \text{at} \quad z = 0$$

Solution:

$$n(z, t) = \frac{s}{\sqrt{t}} \int_{-\infty}^t \exp(-s^2 t'^2) n(z, t - t') dt'$$

$$n(z, t) = \frac{n_0}{2} \exp\left(-\frac{z^2}{4D_t t}\right) \times \left[ e^{-z} \operatorname{erfc}\left(\frac{z - \sqrt{4D_t t}}{\sqrt{4D_t t}}\right) + e^z \operatorname{erfc}\left(\frac{z + \sqrt{4D_t t}}{\sqrt{4D_t t}}\right) \right]$$

$$D_t = \frac{1}{t} \int_0^t D(t') dt', \quad s = \frac{2\sqrt{\ln 2}}{t_{1/2}}$$

## Diffusion: $S=0, \gamma_3 n^3 \cong \lambda n, z=0$

Diffusion equation:

$$\frac{n}{t} = D(t) \frac{\partial^2 n}{\partial z^2} - n + \frac{n_0 s}{\sqrt{t}} e^{-z - s^2 t^2}$$

Initial/boundary conditions:  $n(z, t) = 0$  at  $t = -\infty$

$$\frac{\partial n}{\partial z} = 0 \quad \text{at } z = 0$$

Solution:

$$n(0, t) = \frac{s}{\sqrt{t}} \int_{-\infty}^t e^{-s^2 t'^2} n(0, t - t') dt'$$

$$n(0, t) = n_0 \exp\left(-\frac{z^2}{4D_t t} - st\right) \operatorname{erfc}\left(\frac{z + \sqrt{4D_t t}}{\sqrt{4D_t t}}\right)$$

$$D_t = \frac{1}{t} \int_0^t D(t') dt', \quad s = \frac{2\sqrt{\ln 2}}{t_{1/2}}$$

# Diffusion

Diffusion equation:

no drift term

$$\frac{\partial n}{\partial t} = D(t) \frac{\partial^2 n}{\partial z^2} - n + \frac{n_0 s}{\sqrt{t}} e^{-z^2/s^2 t}$$

Initial/boundary conditions:  $n(z, t) = 0$  at  $t = -\infty$

$$\frac{\partial n}{\partial z} = 0 \quad \text{at } z = 0$$

Diffusivity:

(Smirl, 1984)

$$D_{\text{amb}} = 2 \frac{D_e D_h}{D_e + D_h}$$

$$D(T_L, T_c) \propto T_L^{-1} \sqrt{T_c}$$

At 300 K:  $D_{\text{amb}} = 67 \text{ cm}^2/\text{s}$  (Wang, 1989).

Here: consider hot carriers, neglect non-equilibrium phonons.

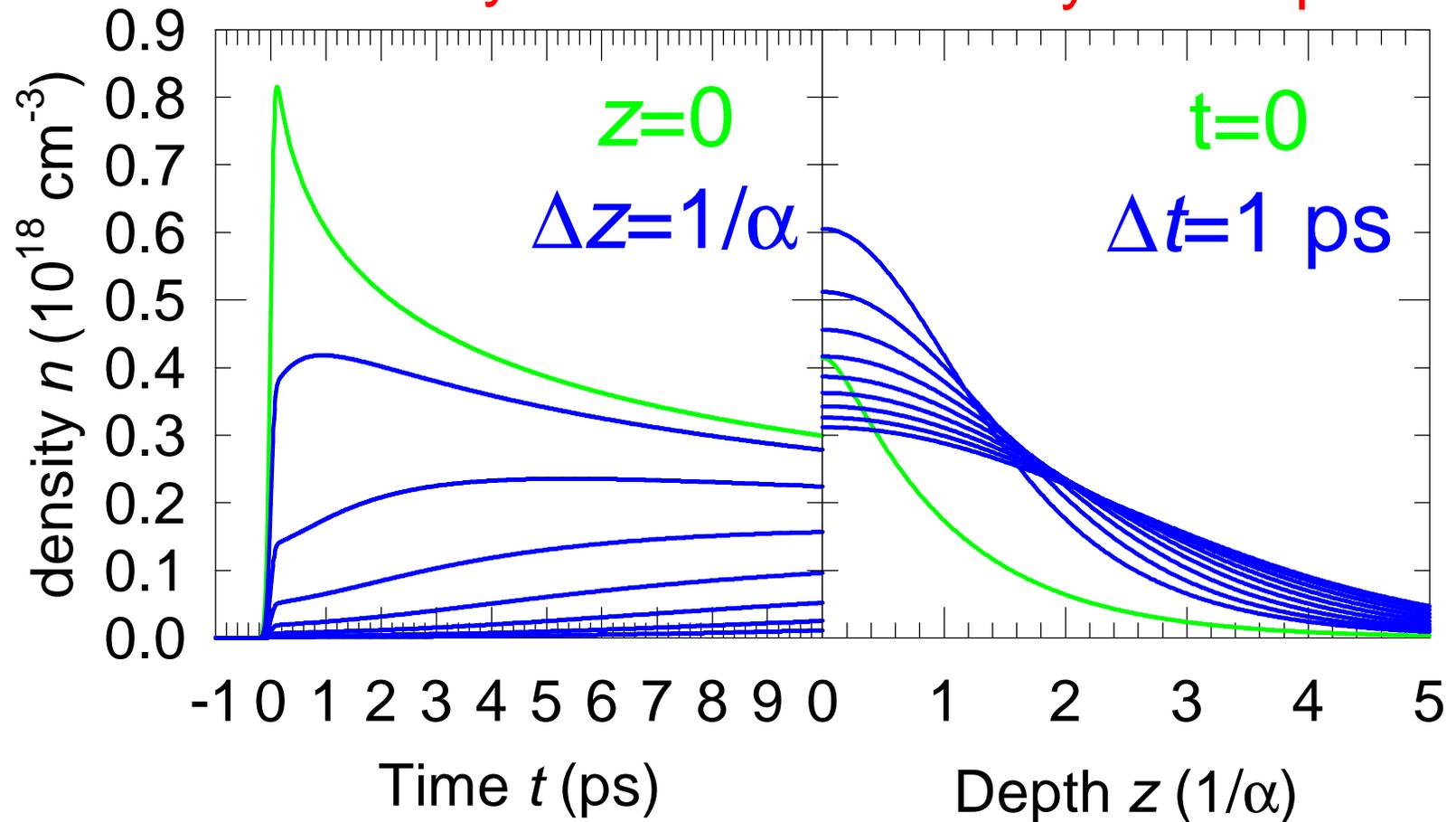
$\Rightarrow D_{\text{amb}}(t) \leq \underline{\underline{134 \text{ cm}^2/\text{s}}}$  corresponding to  $T_c = 1200 \text{ K}$ .

# Diffusion

( $D=134 \text{ cm}^2/\text{s}$ )

Density vs. time

Density vs. depth

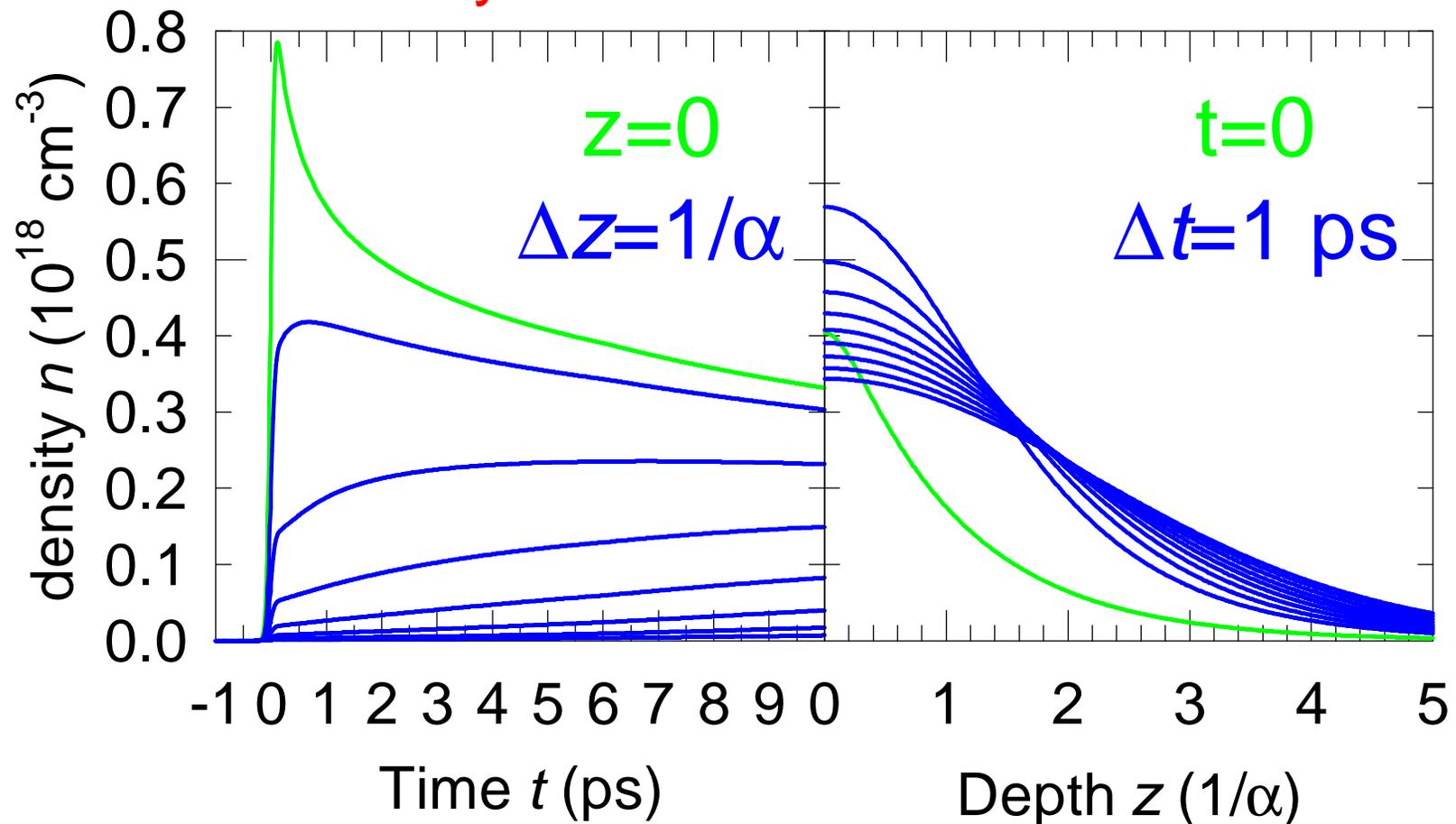


# Diffusion

$D(t)$  from Monte Carlo simulation

Density vs. time

Density vs. depth



## Plasma Oscillations (Drude Model):

- 140 fs laser pulse creates free carriers:  $n_0 = 10^{19} \text{ cm}^{-3}$ .
- Forced plasma oscillations (electrons/holes):

$$\frac{qE_0}{m} \cos t = \ddot{x} + \dot{x} + \frac{2}{p}x$$

- **Plasma frequency:**  $\omega_p = 2.1 \times 10^{14} \text{ s}^{-1}$  (electrons,  $\mu = 0.044$ ).
- **Laser frequency:**  $\omega_L = 2.3 \times 10^{15} \text{ s}^{-1}$  ( $h\omega_L = 1.5 \text{ eV}$ ).
- **$\tau = 1/\gamma$  relaxation time:**  $ne^2\tau/\mu = \sigma = \epsilon_0\epsilon_2\omega_L$ .  
 $\mu = 0.044$ ,  $\epsilon_2 = 2.8$ ,  $\tau = 8.8 \text{ fs}$ ,  $\omega_L\tau = 20 \gg 1$ .
- **critical damping:**  $\gamma/\omega_p = 2$ ; here:  $\gamma/\omega_p = 0.5 = (\omega_p/\omega_L)(\epsilon_s/\epsilon_2)$ .
- **Forced plasma oscillations with frequency  $\omega_L$  and 8.8 fs relaxation time (small damping).**

# Drude dielectric function

■ plasma frequency:  
(time-dependent)

$$\omega_p^2(t) = \frac{n(t)e^2}{\epsilon_0 m_e}; \quad \omega_p(0) = 2.1 \times 10^{14} \text{ s}^{-1}$$

■ effective mass:  
(time-dependent)

$$\frac{n(t)}{m(t)} = \sum_e \frac{n_e(t)}{m_e} + \sum_h \frac{n_h(t)}{m_h}$$

■ dielectric function changes:

$$\Delta \epsilon_L(\omega) = - \frac{ne^2}{\epsilon_0 \left( \omega^2 + i \gamma \omega \right)}$$

■ real part:

$$\Delta \epsilon_1(\omega) = - \frac{\omega_p^2}{\omega^2 + \gamma^2} \approx - \omega_p^2 \left( \frac{1}{\omega^2} \right) = - \frac{\omega_p^2}{\omega^2}$$

■ imaginary part:

$$\Delta \epsilon_2(\omega) = \frac{\omega_p^2 \gamma}{\omega \left( \omega^2 + \gamma^2 \right)} = - \Delta \epsilon_1(\omega) \frac{\gamma}{\omega} \approx 0$$

## Reflectivity changes

- Reflectivity  
(at normal incidence):

$$R = \left| \frac{n-1}{n+1} \right|^2 = \left| \frac{\sqrt{\epsilon} - 1}{\sqrt{\epsilon} + 1} \right|^2$$

- Reflectivity change:

$$\Delta R = \frac{4 \operatorname{Re}[(\bar{n}^2 - 1)\Delta n]}{|n+1|^4}$$

$$\Delta n = \frac{\Delta}{2n} = \frac{\Delta}{2\sqrt{\epsilon}}$$

- Example:  $n_0 = 10^{19} \text{ cm}^{-3}$

$$h\omega_L = 1.5 \text{ eV}$$

$$\lambda_L = 820 \text{ nm}$$

$$P = 180 \text{ mW}$$

$$r = 27 \text{ } \mu\text{m}$$

$$\mu = 0.089 m_0$$

$$\epsilon = 21.6 + 2.8i$$

$$n = 4.7 + 0.3i$$

$$R = 0.42$$

$$\epsilon_\infty = \epsilon_s = 16$$

$$\alpha = 45 \times 10^3 \text{ cm}^{-1}$$

$$\lambda_p = 220 \text{ nm}$$

$$\Delta \epsilon = -0.068$$

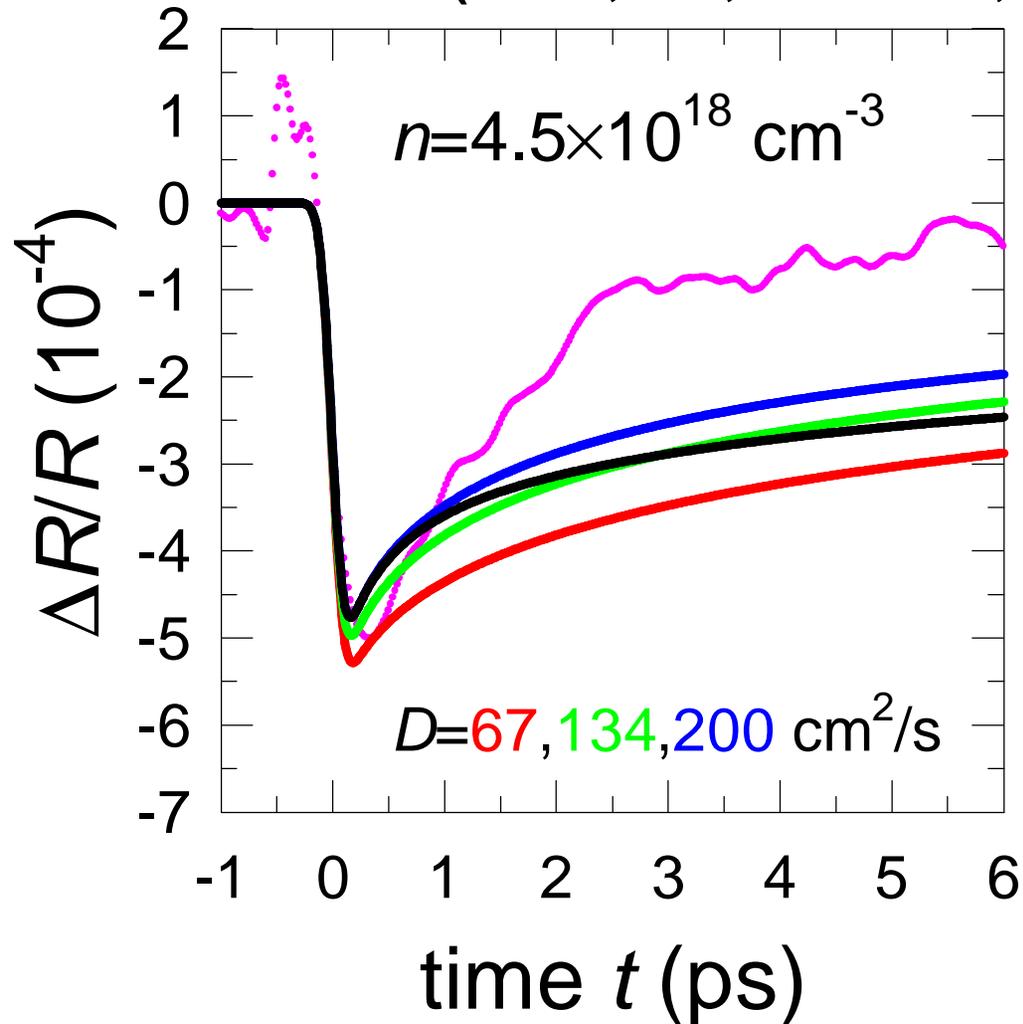
$$\Delta n = (-73 + 5i) \times 10^{-4}$$

$$\Delta R = -6 \times 10^{-4}$$

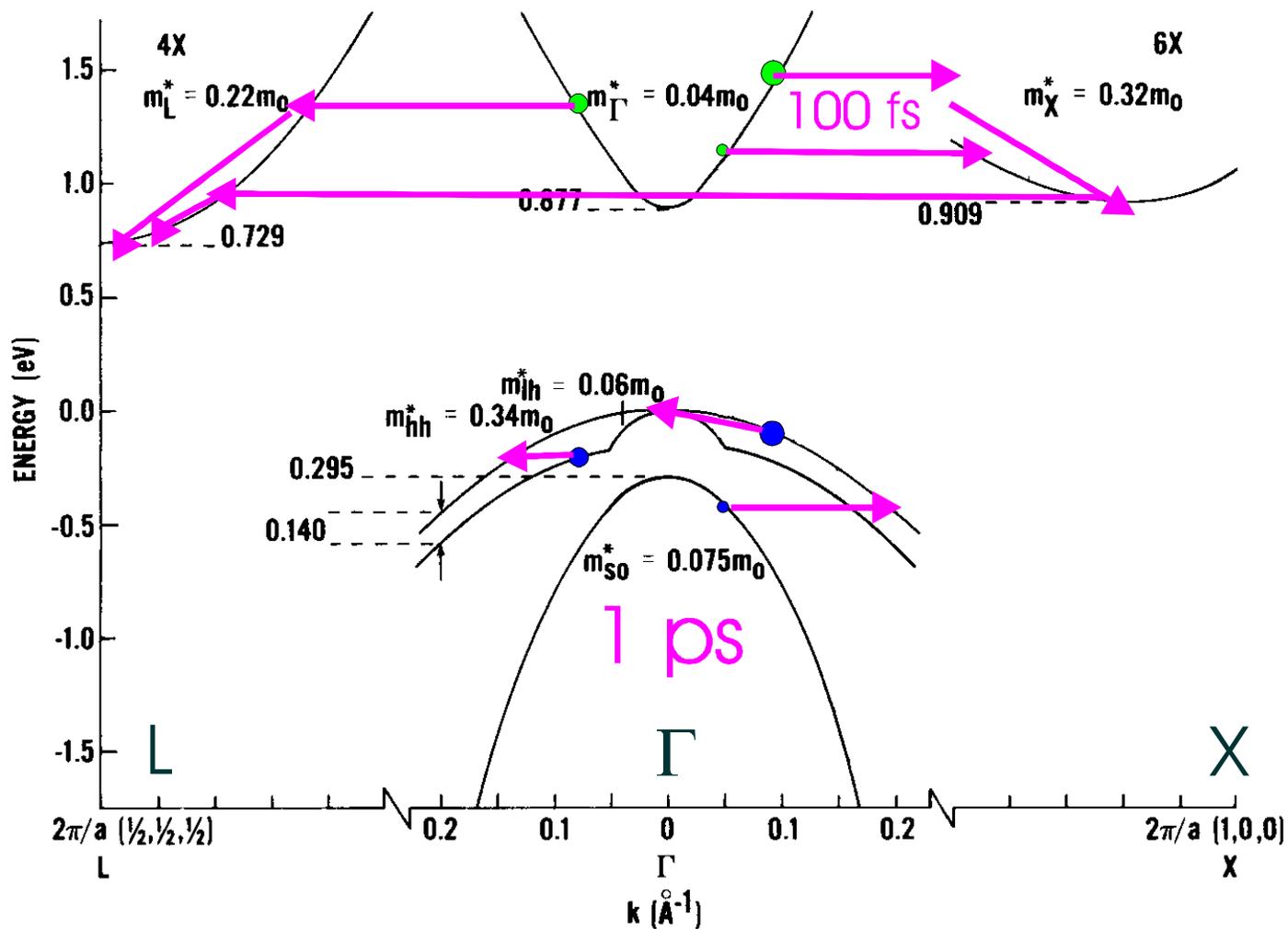
$$\Delta R/R = -13 \times 10^{-4}$$

## Reflectivity change due to diffusion

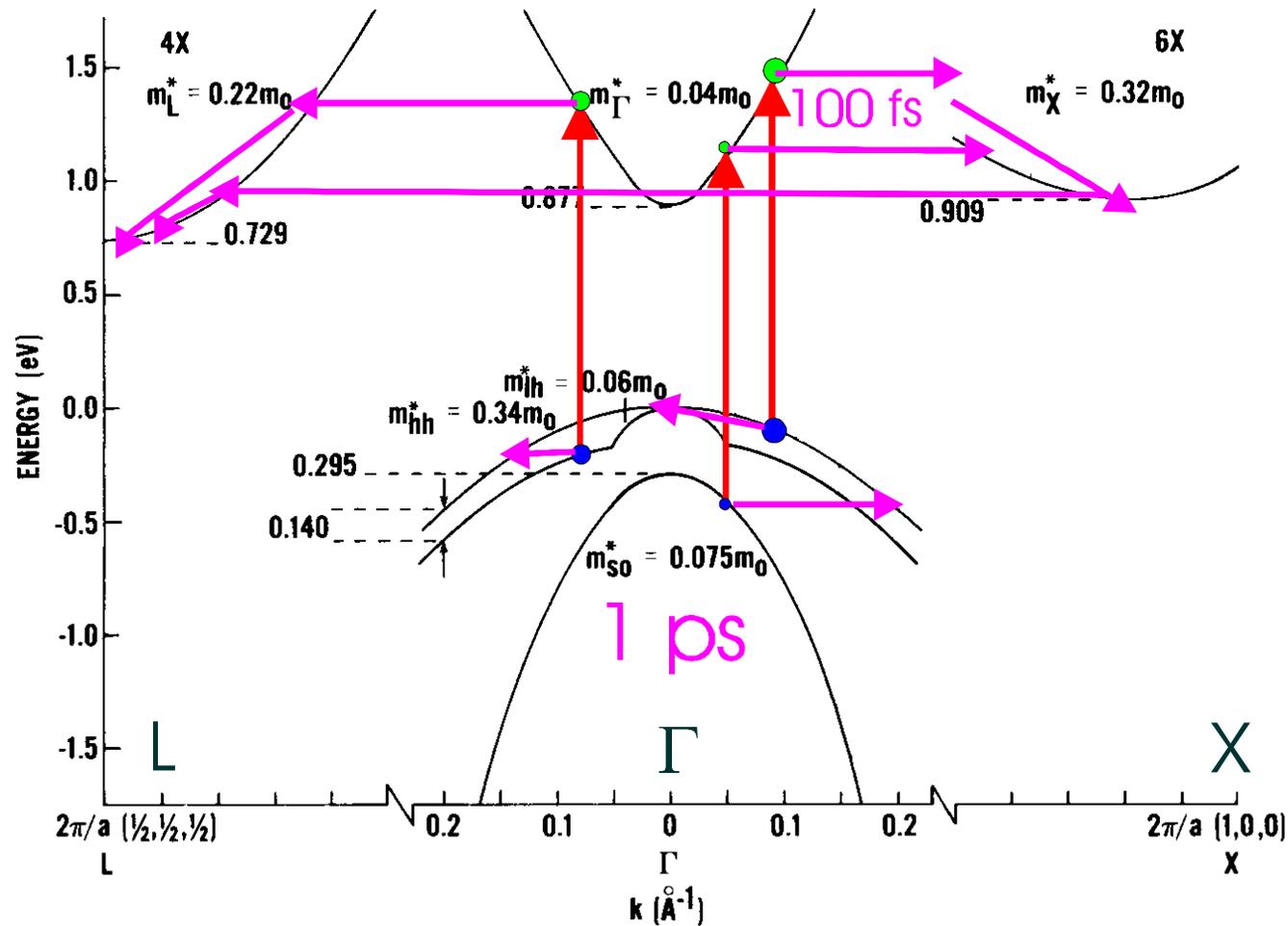
for *L*-electrons and heavy holes  
and different diffusivities ( $D=67, 134, 200$  cm<sup>2</sup>/s, from MC)



# Relaxation of Electrons and Holes



# Photoexcitation and relaxation of electrons and holes

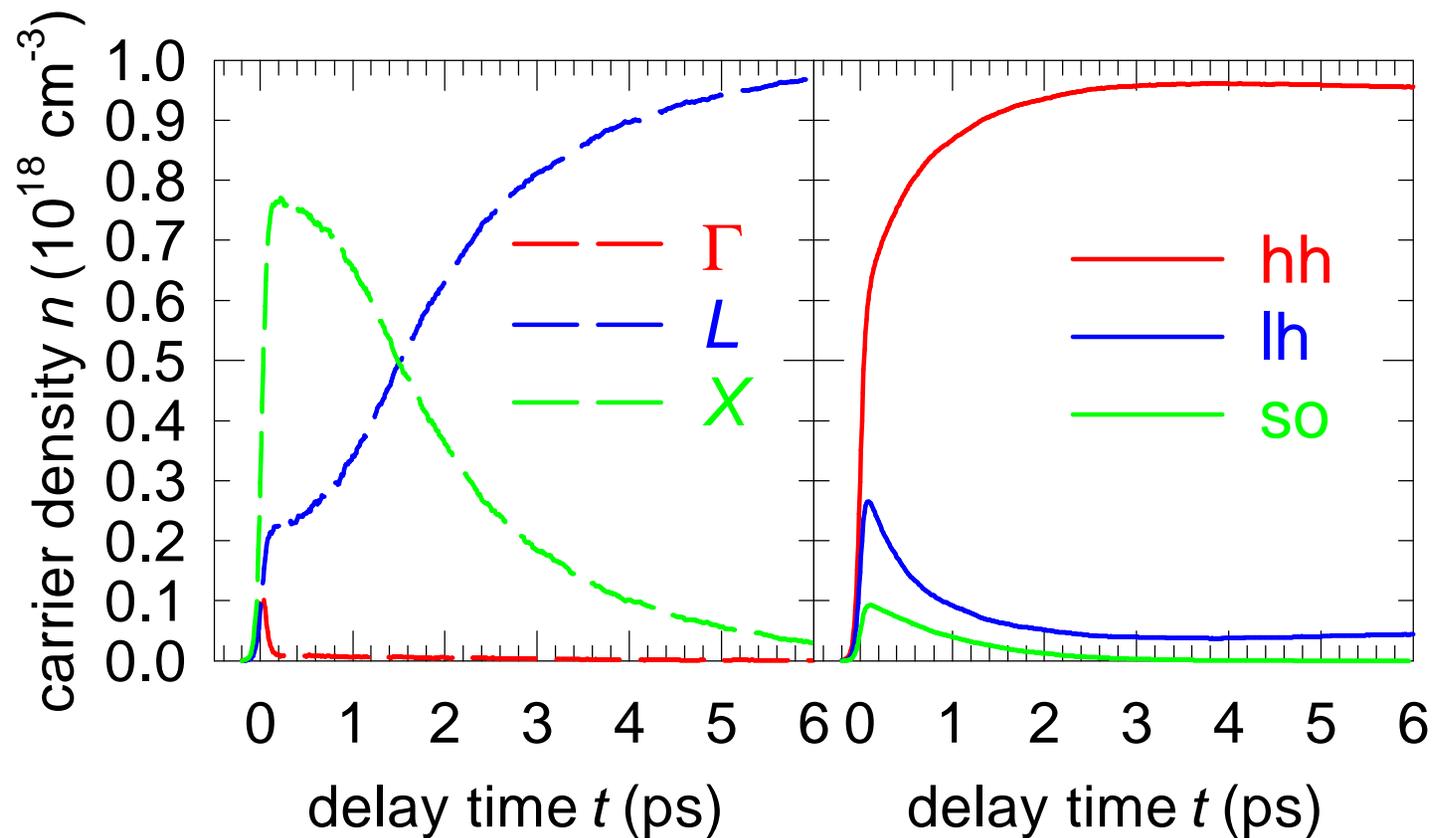


# Monte-Carlo simulation (no diffusion)

D.W. Bailey and C.J. Stanton, J. Appl. Phys **77**, 2107 (1995)

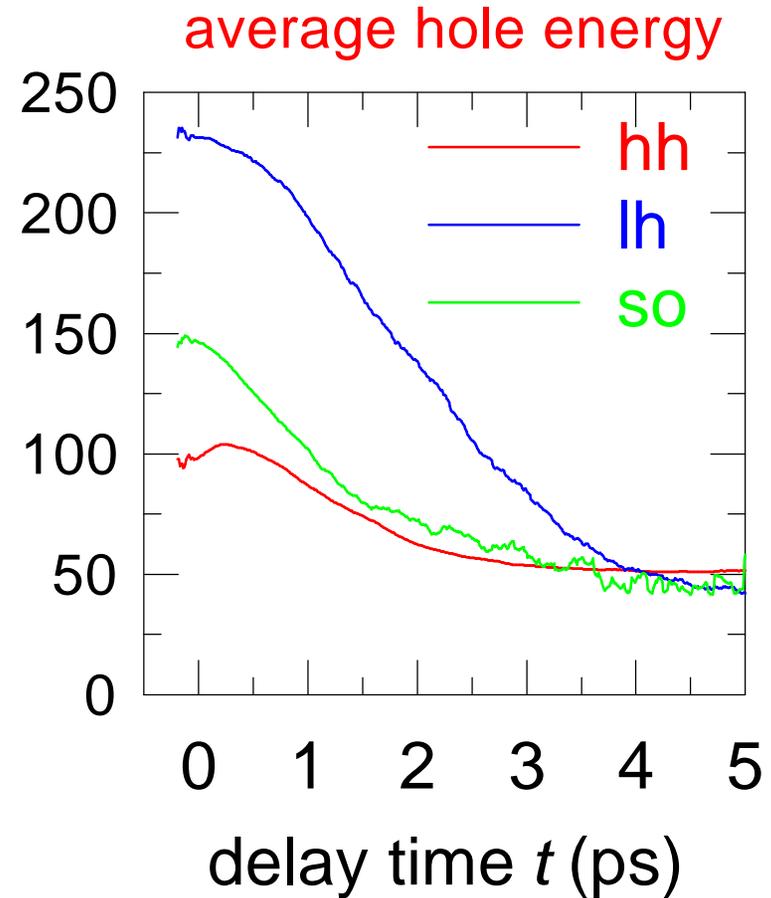
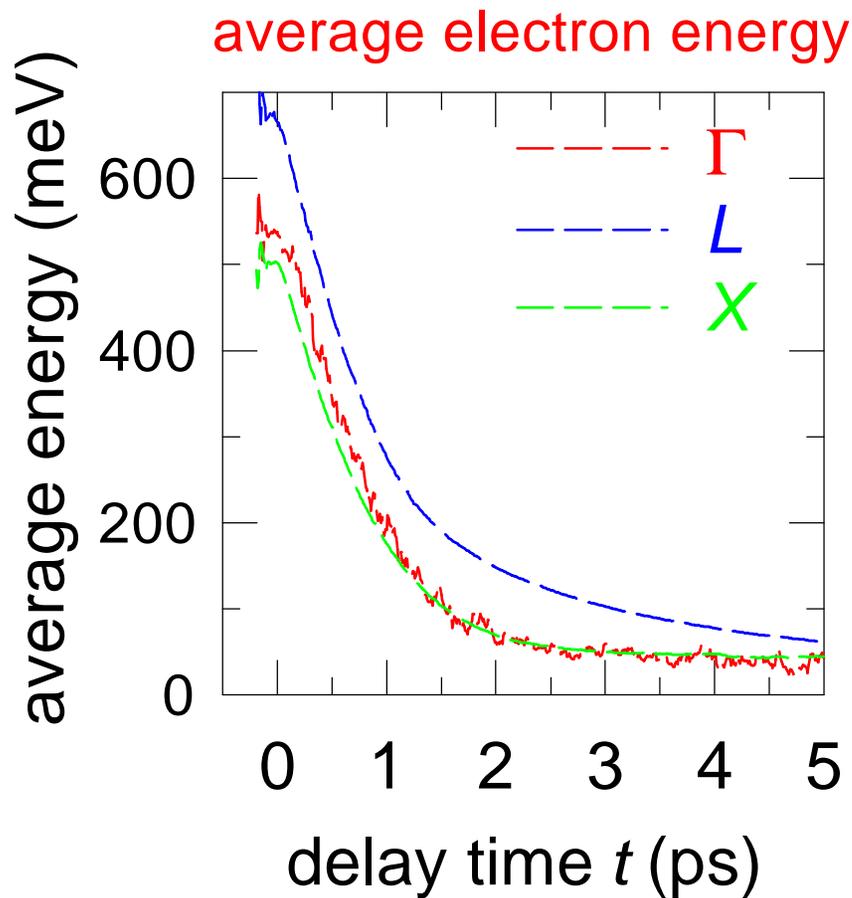
**Electron distribution**

**Hole distribution**



# Monte-Carlo simulation (no diffusion)

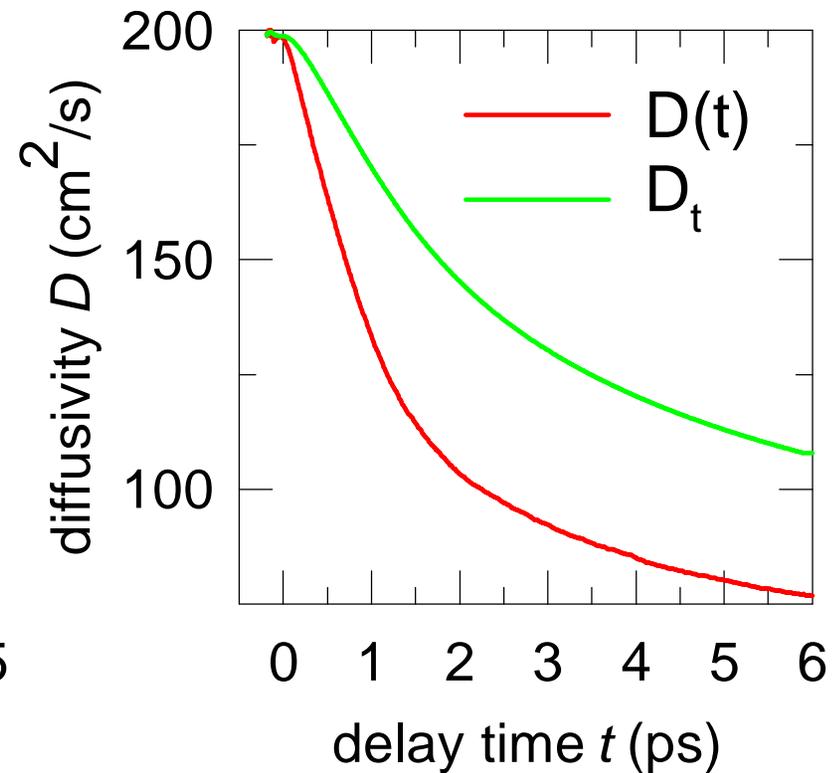
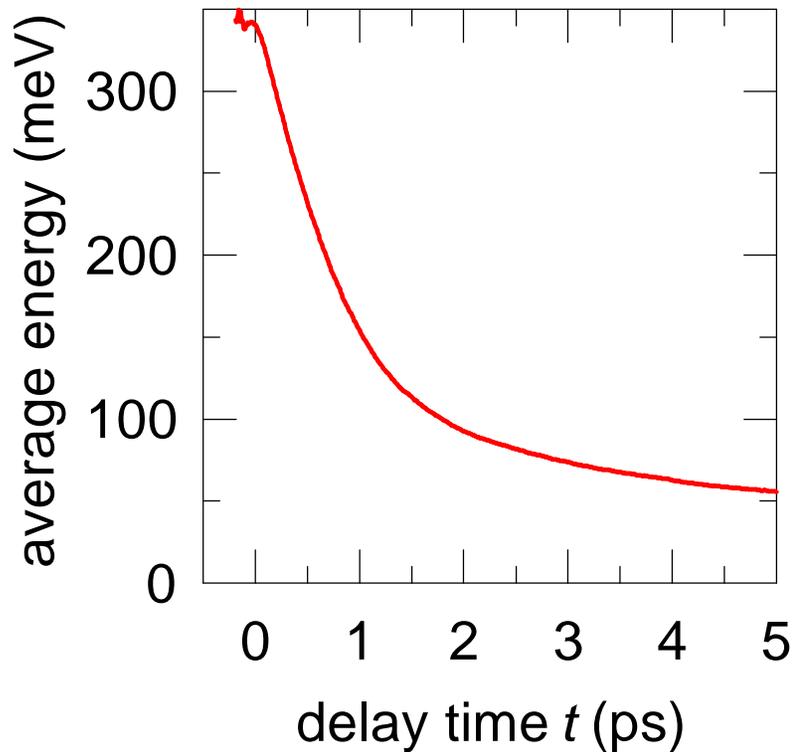
D.W. Bailey and C.J. Stanton, J. Appl. Phys **77**, 2107 (1995)



# Monte-Carlo simulation

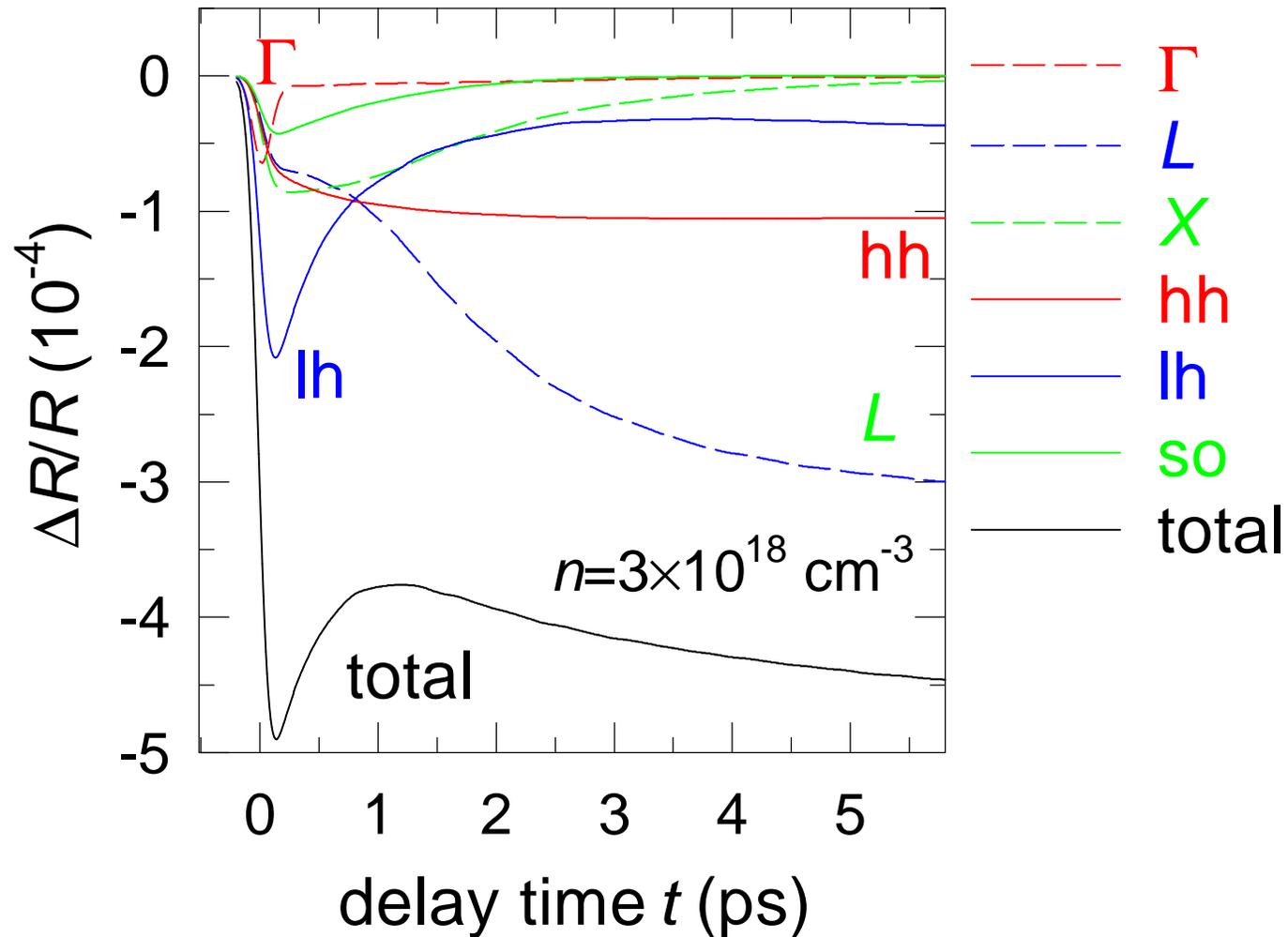
$$D_{\text{amb}}(T_L, T_c) \propto T_L^{-1} \sqrt{T_c} \text{ (Smirl, 1984)}$$

$$D_{\text{amb}}(t) = 67 \text{ cm}^2/\text{s} \times \sqrt{\frac{2E_{\text{ave}}(t)}{3k_B \times 300 \text{ K}}}$$

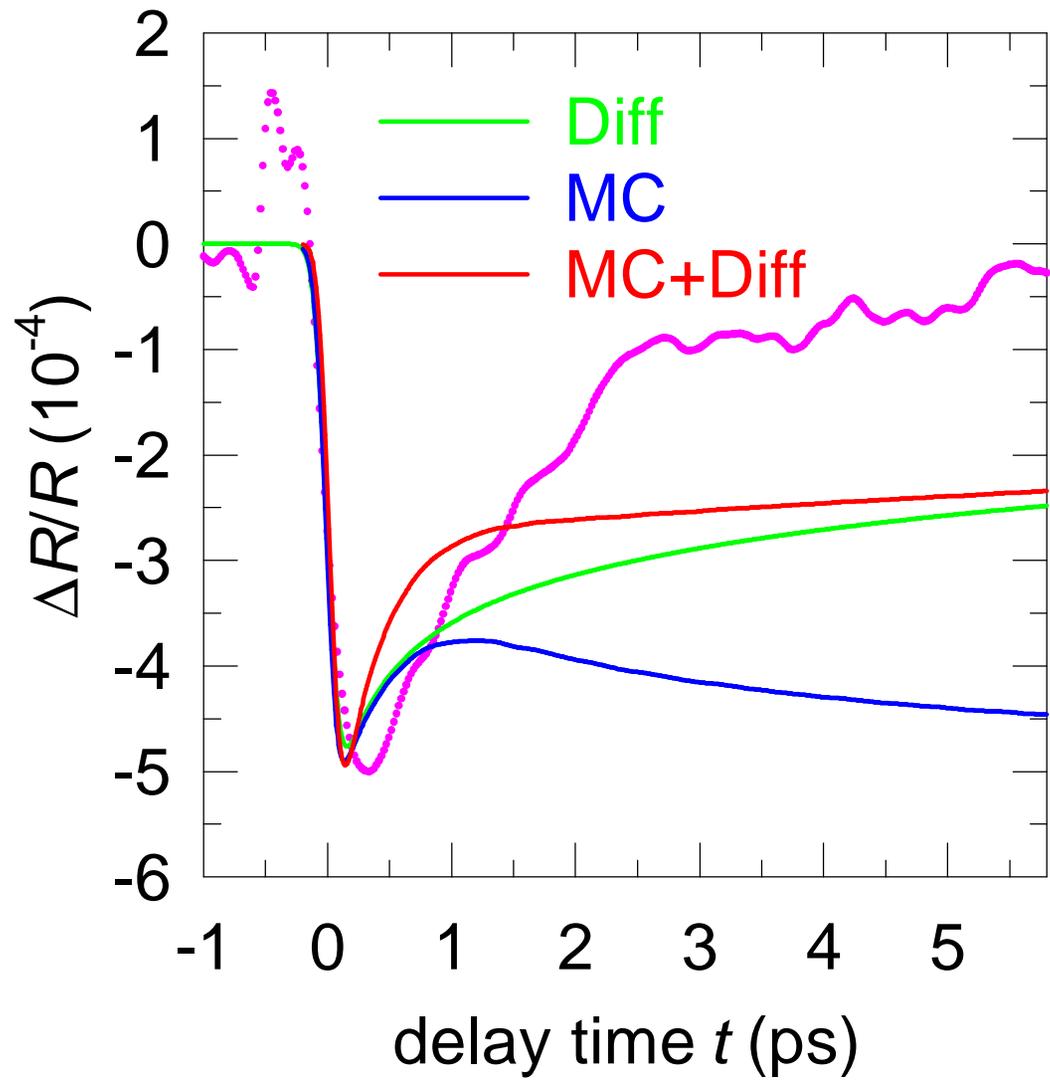


# Monte-Carlo simulation (no diffusion)

## Reflectivity contributions from different bands



# Diffusion plus Monte-Carlo ( $n=4 \times 10^{18} \text{ cm}^{-3}$ )



# Bandgap Renormalization

$$E_{e,h}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m_{e,h}} + \text{Re} \Sigma_{e,h}(\mathbf{k}, E_{e,h}(\mathbf{k}))$$

- $\Sigma$  single-particle energy (dynamically screened Coulomb-interaction, Pauli exchange)
- rigid shift of the valleys ( $\Sigma$  is  $k$ -independent)
- Band gap renormalization:  $\Delta E_g = \Sigma_e + \Sigma_h$
- **Problem 1:** Multicomponent plasma: electrons near  $\Gamma$ , L, and X, holes near  $\Gamma$  (see Kalt and Rinker, 1992).
  - Coulomb-exchange: all components affected.
  - Correlation (Pauli): within same component.
- **Problem 2:** Plasma is NOT in thermal equilibrium

# Bandgap renormalization: T=0, k=0, E=0

**Universal relationship** (Vashista/Kalia, Zimmermann):

$$E_{xc}(r_s) = \frac{a + br_s}{c + dr_s + r_s^2} E_X = -14E_X = -25 \text{ meV}$$

$$\Delta E_g = E_{xc}(r_s) + n \frac{E_{xc}}{n} = -3.24r_s^{-3/4} E_X = -29 \text{ meV (dir) or } -38 \text{ meV (ind)}$$

$$\Delta R = - \frac{R}{(h)} \Delta E_g = 26 \times 10^{-4} \text{ (direct) or } 34 \times 10^{-4} \text{ (indirect)}$$

	$n=10^{19} \text{ cm}^{-3}$	<b>direct</b>	<b>indirect</b>	<b>E<sub>1</sub> (2D)</b>
<b>exciton binding energy</b>	$E_X = 13.6 \text{ eV} \times \frac{1}{2}$	1.8 meV	4.1 meV	13 meV
<b>Bohr radius</b>	$a_B = 0.53 \text{ \AA} \times \frac{1}{s}$	250 \AA	115 \AA	71 \AA
<b>interparticle distance</b>	$r_s = \sqrt[3]{\frac{3}{4} \frac{1}{n a_B}}$	0.12	0.25	0.41

## 3D-Kepler problem (Hydrogen atom)

$$\left[ \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + \frac{e^2}{(x^2 + y^2 + z^2)} + E \right] \Phi(x, y, z) = 0$$

$$\text{Energy: } E_n = -\frac{1}{n^2} E_0 = -\frac{1}{n^2} \times 13.6 \text{ eV}, \quad n = 1, 2, 3, \dots$$

$$\text{Radius: } a_n = n a_0 = n \times 0.529 \text{ \AA}, \quad n = 1, 2, 3, \dots$$

## 2D-Kepler problem (pancake exciton)

$$\left[ \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{e^2}{(x^2 + y^2)} + E \right] \Phi(x, y) = 0$$

$$\text{Energy: } E_n = -\frac{1}{n^2} E_0 = -\frac{1}{n^2} \times 13.6 \text{ eV}, \quad n = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$$

$$\text{Radius: } a_n = n a_0 = n \times 0.529 \text{ \AA}, \quad n = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$$

$$\text{2D - Rydberg: } \text{Ry}^* = -54.4 \text{ eV}, \quad \text{2D Bohr radius: } a_B = 0.265 \text{ \AA}$$

## 3D indirect exciton

Binding Energy:  $E_X = -\frac{1}{2s} \times 13.6 \text{ eV} = -4.7 \text{ meV}$

Bohr radius:  $a_B = \frac{1}{s} \times 0.529 \text{ \AA} = 95 \text{ \AA}$

## 2D E<sub>1</sub> "pancake" exciton

transverse mass:  $m^* = 0.06$

Binding Energy:  $E_X = -\frac{4}{2s} \times 13.6 \text{ eV} = -13 \text{ meV}$

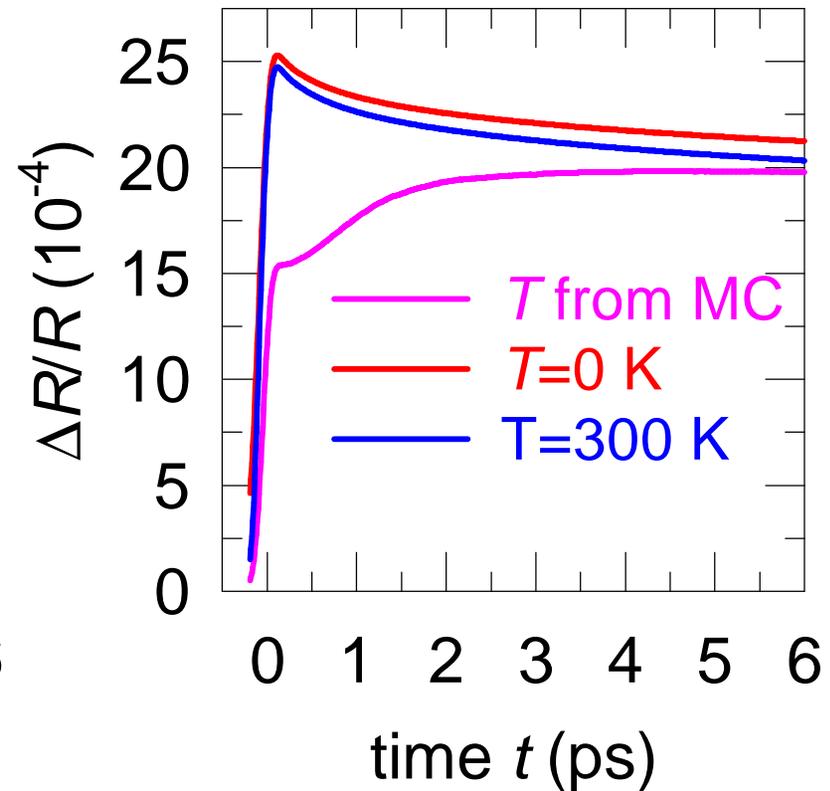
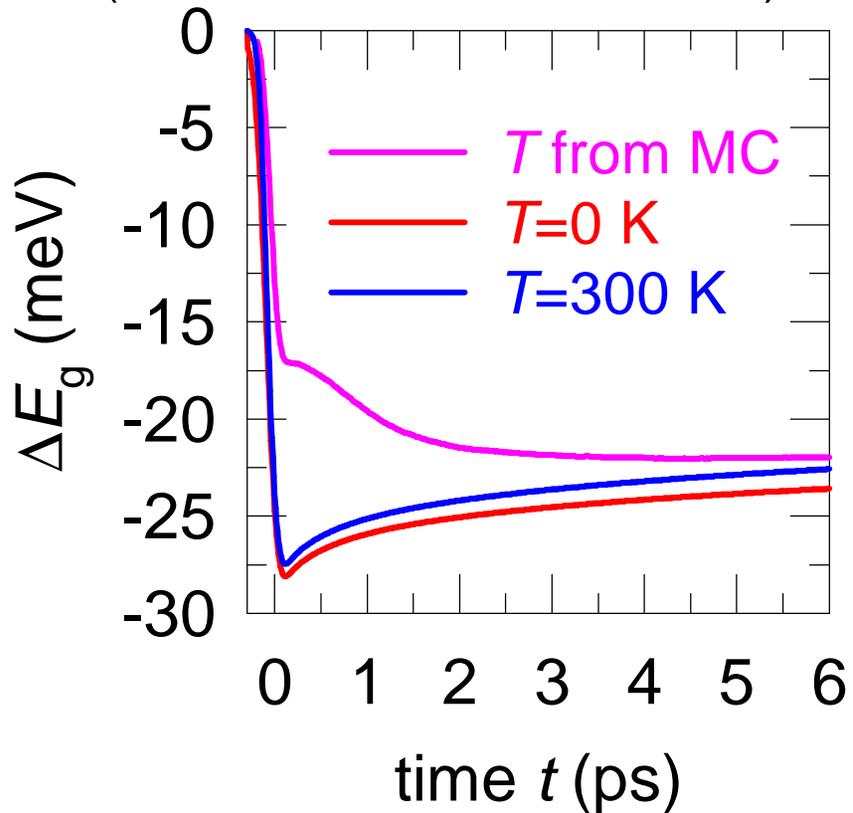
Bohr radius:  $a_B = \frac{1}{2s} \times 0.529 \text{ \AA} = 71 \text{ \AA}$

# Bandgap renormalization: $T > 0, k = 0, E = 0$

- Temperature scale:
- BGR (Zimmermann):  
(indirect exciton, all carriers)

$$= \frac{kT}{E_x} = \frac{2E_{\text{ave}}}{3E_x}$$

$$\Delta E_g = - \frac{3.24 r_s^{-3/4}}{(1 + 0.047 r_s^3)^{1/4}} E_x$$



# Accumulation of Carriers

- Diffusion equation:  $0 = \frac{dn}{dt} = D \frac{d^2n}{dz^2} - n + e^{-z}$   
(steady-state)  
no surface recombination  $= n_0 f_{\text{rep}}$
- boundary condition:  $\frac{dn}{dz} = 0$  at  $z = 0$
- Solution:  $n(z) = \frac{n_0 f_{\text{rep}}}{D^{-2} - 1} \left[ \sqrt{\frac{D^{-2}}{1 - D^{-2}}} \exp\left(-\sqrt{\frac{z}{D}}\right) - \exp(-z) \right]$   
 $n(z=0) = \frac{n_0 f_{\text{rep}}}{D^{-2} - 1} \left[ \sqrt{\frac{D^{-2}}{1 - D^{-2}}} - 1 \right] \approx n_0 \frac{f_{\text{rep}}}{\sqrt{D^{-2}}}$
- **Auger recombination rate:**  $\lambda = 400$  ns @  $4 \times 10^{18}$  cm<sup>-3</sup>  
(Smirl, 1984)
- **carrier accumulation:**  $n_{\text{acc}}/n_0 = 18\%$ .

# Bandgap renormalization

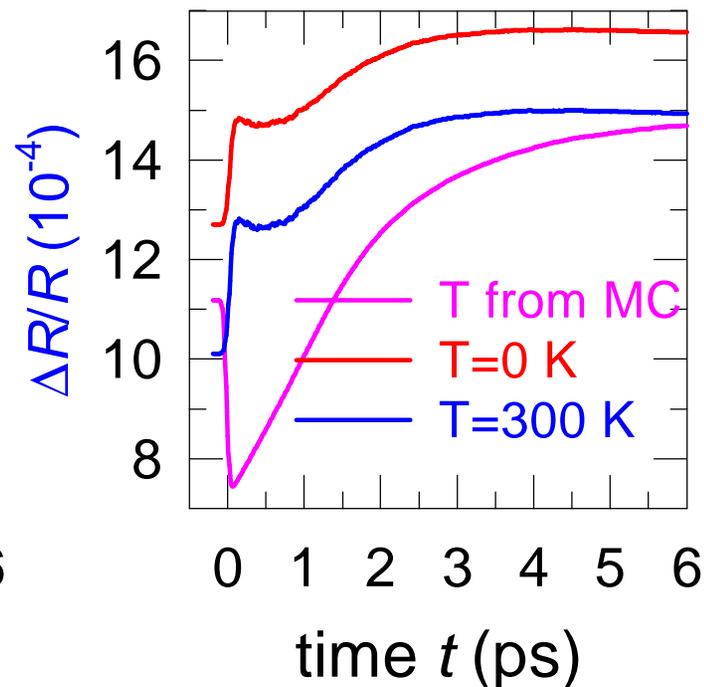
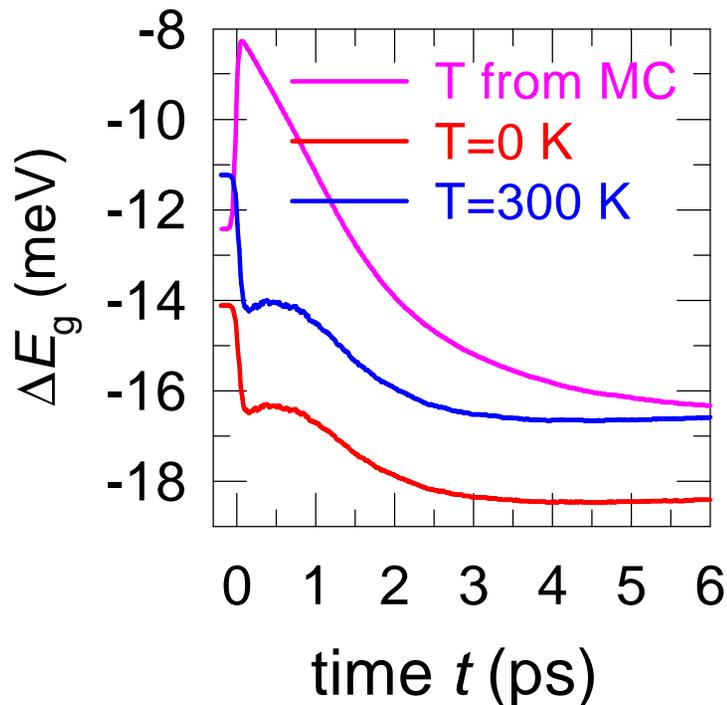
(with accumulation of carriers at 20%)

- Temperature scale:

$$= \frac{kT}{E_x} = \frac{2E_{\text{ave}}}{3E_x}$$

- BGR (Zimmermann):  
(indirect exciton, 4 L-valleys)

$$\Delta E_g = - \frac{3.24 r_s^{-3/4}}{(1 + 0.047 r_s^3)^{1/4}} E_x$$

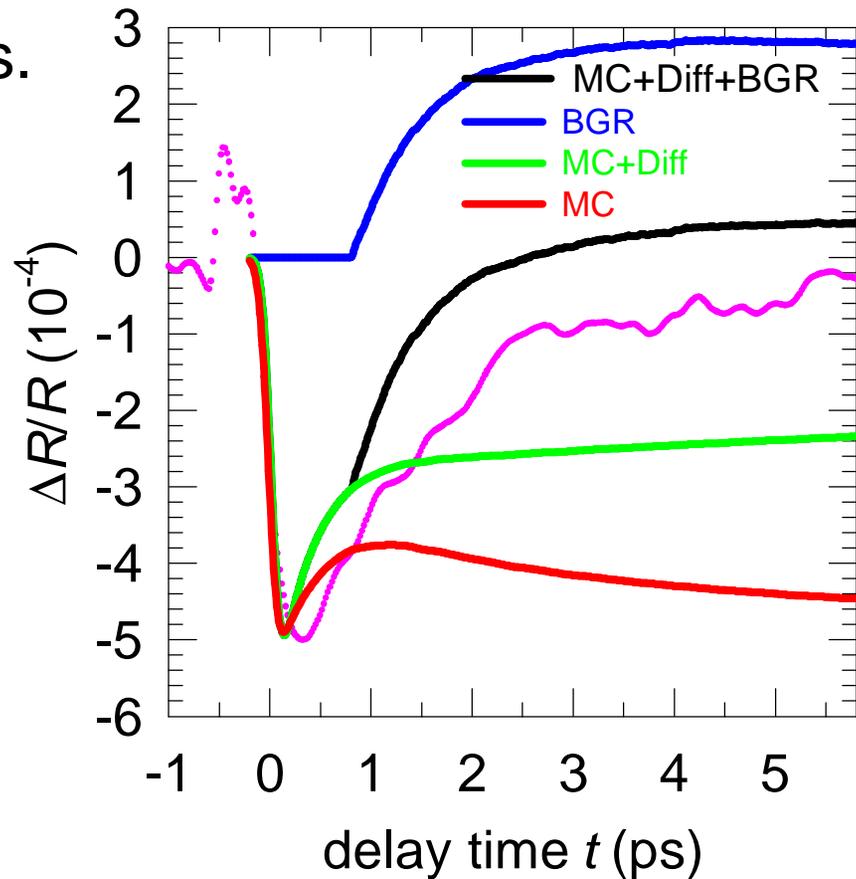


## Adding it all up

- MC: distribution and energies (temperature).
- $T$ -dependent diffusivity.
- $T$ -dependent band gap renormalization.
- accumulation of carriers.
- no screening at  $t=0$ .
- heavy-hole to light hole scattering:

$$d_0 = 30..35 \text{ eV}$$

(Cerdeira, Cardona, 1972)



## Conclusions:

- Transient photo-induced reflectivity changes ( $\Delta R/R$ ) for Ge, 140 fs resolution, 1.5 eV.
- Drude-response to  $\Delta R/R$  is mostly due light holes.
- We have considered:
  - diffusion away from the surface,
  - relaxation of electrons and holes (MC simulation),
  - band-gap renormalization.
- Because of the unique band structure of Ge, we are able to study, for the first time, the dynamics of the holes, particularly the scattering of light holes to the heavy hole band (optical DP  $d_0=30..35$  eV).